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SEA WATER CONVERSION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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"Study of Permeability Characteristics of Membranes"

Quarterly Report No. 6
Covering Period February 9 - May 9, 1969

K. S. Spiegler, Principal Investigator
J. C. T. Kwak
D. A. Zelman
J. Leibovitz (part time)

Contract No. 952109
Jet Propulsion Laboratory
Pasadena, California

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Table of Contents

	page
Abstract	iv
I. Introduction	1
II. The Concentration Feedback System.	2
III. Preliminary Volume Flow Experiments.	4

Abstract

Some volume flow measurements across the AMF C-103 cation-exchange membrane under the influence of osmotic and pressure forces are reported. The effect of small volume losses from the cell compartments on the osmosis and hyperfiltration experiments is evaluated. An experimental procedure was worked out which will enable us to correct for the leak rate even in experiments where osmotic flow is taking place. Some improvements in the switching mechanism of the concentration feedback system and new conductivity cells are described.

I. Introduction

This is the sixth quarterly report of a research program designed to (a) construct one apparatus in which transport of salt, ions and water across membranes can be determined with differences in concentration, electric potential and pressure as driving forces, together with the measurement of membrane and streaming potential, and (b) perform a variety of transport measurements in it to determine the range in which linear relationships between fluxes and forces exist. This will permit us to study the performance of separators and membranes from a minimum number of basic characterization measurements.

The experimental system has been described in the first annual report (November, 1968). Some minor alterations are reported here, together with the results of some preliminary experiments. In Quarterly Report No. 5 (February, 1969) the problem of small volume losses from the cell was described and some improvements in the assembly of the cell were reported. The main effort in the period covered by this report has been directed towards the detection, measurement and elimination of leaks or apparent leaks. Preliminary pressure flow experiments were performed in the course of these leak detection and measurement efforts. The results of these experiments will not be used in the evaluation of the final results of this program, but they enabled us to study and minimize the effect of volume losses and to develop a practical and reliable experimental procedure. Because of the difficulties encountered with the volume losses from the cell, there has been a delay in starting complete series of transport experiments. However, experiments are now under way and the first results will be described in the forthcoming progress reports.

II. The Concentration Feedback System

The concentration feedback mechanism, designed to keep the concentration in each cell half constant while actual salt and water transport through the membrane takes place, operates as follows (see the First Annual Report, November, 1968 and the Fifth Quarterly Report, February, 1969, for more details). The resistance of a conductance cell inserted in each compartment of the membrane transport cell is compared with a reference resistance by means of a 1605 AH impedance comparator (General Radio Co., West Concord, Mass.). The differential DC output signal of the comparator is amplified and actuates a very sensitive, polarized MDP 1007 relay (Potter and Brumfeld Div., American Machine and Foundry Co., Princeton, Ind.). In the original setup, this relay activated an AC relay, which in its turn then started an automatic buret, pushing concentrated salt solution into the depleted side. On the enriched side this AC relay started a pump-motor which circulated some of the cell solution through a demineralizing column. As was described in the Fifth Quarterly Report, the instabilities in the comparator readings, due to rapid temperature and concentration fluctuations in the cell solutions, cause the relays to flash on and off when the comparator output is close to the relay actuation threshold. In due time this led to a deterioration of the contacts of the power relay, causing sparking and unstable comparator readings. Since the proper operation of the relays is essential for the desired accuracy, modification of the relay circuits was considered of primary importance and was indeed achieved.

First the AC relays were replaced by Fisher Transistor Relays No. 13-991-80 V2 (Fisher Scientific Co., Pittsburgh, Pa.) which are triggered when the input is short-circuited with a resistance of up to 10^6 Ohm. The electronic circuit of the relay was altered in such a way that delay times

of 2 seconds when switching on and of 0.5 seconds when switching off were introduced. Although this prevented the oscillations of the feedback system experienced earlier, a sharp disturbance of the comparator reading was still found at the moment of switching. In order to correct this effect S6W6P contact protectors (International Rectifier Company, El Segundo, Calif.) were connected to the relay contacts of the Fisher electronic relay. These protectors proved to prevent any sparking and thus a stable comparator reading during switching is obtained. Together with the switching delays this provides for a very smooth and reliable performance of the feedback switching system.

New conductivity cells were constructed and inserted in the transport cell compartments. The new cells are made of glass and have a cell constant of about 6. They are open to the inside of the transport cell, thus permitting a fast response of the resistance reading to concentration changes in the cell solution, which is essential for the operation of the feedback system. These glass cells are preferred over the original plastic cells because no deformation under internal pressure, and subsequent relaxation of the plastic when the internal pressure is taken off, can occur.

III. Preliminary Volume Flow Experiments

Extensive leak testing experiments have been carried out in the first months covered by this report. Because of the low flow rates expected for the ion-exchange membranes under pressure and/or osmotic forces, only very low volume losses can be allowed.

In most osmosis-dialysis or hyperfiltration experiments, flow rates between 10 and 100 $\mu\text{l}/\text{hr}$ are expected for the approximately 7.8 cm^2 exposed membrane area. This means that if the leak rate is lower than $1 \mu\text{l}/\text{hr}^*$, and constant in time within 10%, an error in the flow rate of less than 1% is introduced in the least favorable case.

Preliminary electroosmosis-electromigration experiments were described in the Annual Report (November, 1969). It was found that for the AMF C-103 cation-exchange membrane (American Machine and Foundry Company, Springdale, Conn.), bounded by 0.2 M and 0.05M NaCl solutions, the transport number of Na^+ is between 0.98 and 1.00. The water transport number was found to be about 7.0 moles of H_2O per Faraday transported. These preliminary results are in good agreement with literature values. [See e.g. E.M. Scattergood and E.N. Lightfoot, Trans. Far. Soc. 64, 1135 (1967).] Low-flow osmosis and hyperfiltration experiments were performed in order to determine the constancy of the leak rate in time and to check the possibility of correcting the observed volume flows for the leak rate as measured in advance.

In a typical experiment, with $c' = 0.1\text{M}$ NaCl and $c'' = 0.08\text{M}^{**}$ NaCl the following results for the volume flow (measured at the low pressure side) were obtained:

$$\begin{array}{lll} p'' - p' = \Delta p = 0 \text{ atm.} & J_V = -5.21 \pm 0.05 \mu\text{l}/\text{hr} \\ \Delta p = -0.48 \text{ atm.} & J_V = -1.2 \pm 0.10 \mu\text{l}/\text{hr} \\ \Delta p = -0.98 \text{ atm.} & J_V = +3.0 \pm 0.20 \mu\text{l}/\text{hr} \\ \Delta p = -1.49 \text{ atm.} & J_V = +6.94 \pm 0.20 \mu\text{l}/\text{hr} \end{array}$$

* $1 \mu\text{l} = 10^{-3}$ milliliter

**Primes and double primes denote properties on left and right side respectively. Positive flow is from left to right.

In the measurements with applied pressure, the volume loss at the high pressure side was 15-30% higher than the gain at the low pressure side.

However, the $\Delta p=0$ atm experiment was done after the pressure experiments and the elastic relaxation of the cell at the high pressure side vitiated the results at $\Delta p=0$ for this cell-half. From the figures given above we calculate for the hydraulic permeability $L_p = (2.8 \pm 0.3) \times 10^{-10} \text{ l sec}^{-1} \text{ cm}^{-2} \text{ atm}^{-1}$, a value in reasonable agreement with previous experiments.

Since the osmotic pressure $\Delta\pi$ in this experiment was about 0.45 atm, it is clear that we had a leak rate of about $1 \mu\text{l}/\text{hr}$. This leak rate could not be detected before the experiment because of the osmotic flow taking place. Therefore the following experimental procedure has to be used in all experiments.

1. Both cell-halves are filled with the solution of the low concentration side and the leak rate in each cell-half is measured during at least 24 hours with buret and demineralizing column connected.
2. The amount of salt necessary to reach the desired concentration, is added to the high-concentration side.
3. Samples of solution from each cell-half are taken and the concentration is checked.
4. The transport experiment is performed. In case of hyperfiltration experiments the osmotic flow rate is measured both before and after the pressure experiment.
5. Again solution samples are taken and the final concentration is determined as a check for the concentration constancy.

When performed in this way, the leak rate in each cell-half can be determined before an experiment with the cell in exactly the same condition

as during an experiment. It is for these reasons that our experimental setup is particularly useful. After assembly, the whole system can be allowed to reach a steady state for a considerable period of time without affecting the initial conditions of the experiment. The leak rate usually stabilizes and drops to an acceptable level. During this time, the concentrations are kept constant by the feedback mechanism. Also, once the cell is assembled, a long run of different experiments can be made without taking the cell apart or refilling the cell compartments.